

**PHOTOCATALYTIC NANO-CRYSTALLINE TiO<sub>2</sub> THIN FILMS, METHOD FOR  
PREPARING THE SAME AND USE THEREOF**

Background of the Invention

Field of the Invention

[0001] The invention relates to a method for preparing nano-crystalline TiO<sub>2</sub> thin films, and to environmental applications, particularly to the use of the nano-TiO<sub>2</sub> thin films under ultraviolet irradiation in killing bacteria and viruses in the environment.

Description of the Related Art

[0002] It is always a challenge to remove organic pollutants in air and to kill the bacteria and viruses in the environment in the fields of environmental science and medicine. In modern society, various organic pollutants and a great number of bacteria and viruses fill the crowded offices, shopping malls and public places. The health of people who live and work under such environments will obviously be affected.

[0003] It is known that TiO<sub>2</sub> semiconductors can effectively decompose organic pollutants in air and water under ultraviolet and kill bacteria therein. Therefore, a simple and feasible way is to have nano-crystalline TiO<sub>2</sub> immobilized on the surface of a substrate such as glass, metals and constructive materials, and then expose the substrate under ultraviolet to catalytically kill bacteria.

[0004] There have been many processes disclosed to fix TiO<sub>2</sub> to the substrate of glass, metals and ceramics, such as chemical vapor deposition, magnetic spraying, high speed spinning coating and pyrolysis. TiO<sub>2</sub> thin films prepared by these processes exhibit very poor photocatalytic and antibacterial activities or are easy to peel off from the substrate for the reasons that the TiO<sub>2</sub> thin films have poor crystallinity (even non-crystalline), and poor adhesivity with substrates to which they attach.

[0005] Chinese patent application No. 01128306.8 filed on July 31, 2001 and published as CN 1400186A, on March 5, 2003. As such, this patent application is not believed to qualify as prior art to the present application which has a priority date of October 28, 2002. The application discloses a process for improving photocatalytic activities of TiO<sub>2</sub>

thin films on glass. The process includes preparing a sol gel of  $\text{TiO}_2$ , coating the thin film on glass, treating the thin film using an acid, washing the treated thin film, and drying the thin film. The sol-gel is prepared by hydrolysis of titanium alkoxide. A stabilizer selected from triethanolamine, diethanolamine etc is used in preparation of the sol-gel.

[0006] Chinese patent application No. 01130896.6 filed on August 31, 2001 and published on April 3, 2002, discloses a process for preparing photo-catalysts of Meso- $\text{TiO}_2$  thin films. The process includes preparing a sol gel solution that is made from a titanium alkoxide or a titanium chloride, lower alkanol diethanolamine, water and polyethylene glycol having a molecular weight from 200 to 4,000; coating a thin film on a substrate by spinning coating or dip coating; and drying and calcining the thin film.

[0007] Chinese patent application No. 0110064.8 filed on March 29, 2001 and published on September 12, 2001, discloses a process for preparing a thin film of  $\text{TiO}_2$  on a substrate. The process includes stirring a solution consisting of titanium alkoxide, ethanol amines and ethanol; adding to the solution a fluorine-containing compound or an aqueous solution of transitional metals, and coating a thin film on the substrate.

[0008] It is known that photocatalytic and antibacterial activities, and hydrophilicity of a  $\text{TiO}_2$  thin film are significantly influenced by its phase constitutions, specific surface area, and porous size and distribution. It is understood that the above parameters of a  $\text{TiO}_2$  thin film are affected by the process for preparing the same. Therefore, the process for preparing a thin film will significantly affect the photocatalytic activity of the  $\text{TiO}_2$  thin film. The inventors, after conducting careful investigations, have found out that the reverse micelle technique is an effective method for preparing  $\text{TiO}_2$  thin films with high photocatalytic activities. Moreover, a thin film prepared by the reverse micelle solution shows higher photocatalytic activity than those prepared by other processes in the prior art. The present invention is hereby provided. The  $\text{TiO}_2$  thin film provided by the present invention is suitably used to photocatalytically decompose organic pollutants in air and thereby to kill bacteria and viruses in an environment.

#### Summary of the Invention

[0009] Accordingly, an object of the invention is to provide a method for preparing a  $\text{TiO}_2$  thin film having anti-bacterial, fungicidal, and/or antiviral activities. The method of the invention comprises the steps of:

- a) providing a reverse micelle solution containing highly-dispersed water nano-droplets, which is made from an organic continuous phase, a non-ionic surfactant and water;
- b) adding an alkyl titanate to the reverse micelle solution and subjecting titanium alkoxide to being hydrolyzed in said nano-droplets of the reverse micelle solution to form a  $\text{TiO}_2$ -containing solution;
- c) forming a wet film onto a substrate dipped into the  $\text{TiO}_2$ -containing solution by a dip coating technique; and
- d) drying the wet film and calcining the dried film.

[0010] Another object of the invention is to provide a nano-crystalline  $\text{TiO}_2$  thin film prepared by the process of the invention. Nano-crystalline materials generally are polycrystalline materials that have grain sizes less than one micron, more preferably no more than about 100nm.

[0011] Still another object of the invention is to provide a method for killing bacteria and viruses in an environment, which comprises the steps of:

- a) coating a  $\text{TiO}_2$  thin film containing nano-crystalline  $\text{TiO}_2$  on to a substrate by a reverse micelle method; and
- b) placing said  $\text{TiO}_2$  thin film in the environment under ultraviolet irradiation.

[0012] Compared with the prior art, the invention has many advantages that the  $\text{TiO}_2$  thin film can be formed onto all kinds of substrates in various shapes without any specific manufacturing apparatus; the  $\text{TiO}_2$  thin film can be readily doped with other components by coating essential components for the  $\text{TiO}_2$  thin film of the invention together with the other components; the  $\text{TiO}_2$  particle's size in the thin film can be controlled by changing the molar ratio between the surfactant and water in the reverse micelle solution; the phase constitutions can be controlled by the thermal treatment of the thin film; and the thin film of the invention has a larger specific area and a higher activity of killing bacteria and viruses due to the nano-structure thereof.

### Brief Description of the Drawings

[0013] Fig. 1 is polycrystalline X-ray diffraction patterns of  $\text{TiO}_2$  thin films of the present invention on stainless steel calcined for different periods of time;

[0014] Fig. 2 is X-ray photoelectron spectra of Ti in thin films of the present invention on stainless steel calcined for different periods of time;

[0015] Fig. 3 is X-ray photoelectron spectra of Fe in thin films of the present invention on stainless steel calcined for different periods of time;

[0016] Fig. 4 is a scanning electron microscope image of a thin film of the present invention on stainless steel calcined at  $500^\circ\text{C}$  for 3 hours;

[0017] Fig. 5 shows photocatalytic activities of thin films of the present invention on stainless steel calcined for different periods of time;

[0018] Fig. 6 shows the photo-induced antibacterial effect of thin films of the present invention on stainless steel calcined for different periods of time; and

[0019] Fig. 7 shows hydrophilicity of thin films of the present invention on stainless steel calcined for different periods of time.

### Detailed Description of the Preferred Embodiment

[0020] In the process for preparing  $\text{TiO}_2$  thin films of the invention, organic continuous phases may be liquid non-polar or lower-polar organic solvents at the ambient temperature. Examples of the organic continuous phases may include: unsubstituted alkanes or alkanes substituted with one or more substituents (substituting groups), unsubstituted alkenes or alkenes substituted with one or more substituents, unsubstituted alkynes or alkynes substituted with one or more substituents, and unsubstituted aromatic hydrocarbons or aromatic hydrocarbons substituted with one or more substituents. The substituents or substituting groups used herein includes, but not limited to, lower alkyl, halide, lower alkoxy, cyanide, nitro and the like. The number of the substituents may be from 1 to 3, and preferably it is 1.

[0021] Unless specifically indicated otherwise, alkane, alkene and alkyne used in the invention include both straight chain or branch chain and cyclic alkane, alkene, and

alkyne. In the invention, the continuous organic phase is selected  $C_{3-8}$  alkane, and preferably  $C_{5-6}$  cycloalkane, and more preferably cyclohexane.

[0022] In the invention, non-ionic surfactants used include polyols partial fatty acid esters, poly oxyethylene aliphatic alcohol ether, polyoxyethylene alkyl phenol ether, Triton series. In the invention, Triton series such as Triton X-100 and Triton X-405 are preferably surfactants, of which Triton X-100 is more preferable.

[0023] In the invention, alkyl titanate has the same meaning as "titanium alkoxide". The alkyl titanate according to the invention is selected from those that can be easily hydrolyzed to  $TiO_2$  in the reverse micelles. Alkyl portion in alkyl titanate may be selected from  $C_{1-6}$  alkyl, more preferably from  $C_{2-4}$  alkyl, and most preferably ethyl and isopropyl.

[0024] The concentration of the non-ionic surfactant in the reverse micelle solution is generally from 0.15 to 0.4M, and preferably 0.2M. The concentration of titanium alkoxide in the reverse micelle solution of the invention is generally from 0.1 to 0.4M, and more preferably from 0.2 to 0.3M. The molar ratio of water to the surfactant used in the invention may be between 1.0 and 3.0.

[0025] In addition, a small amount of a stabilizer can be added to the reverse micelle solution to control the rate of hydrolysis of the titanium alkoxide. In the invention, organic compounds of 2,4-diketone may be used as the stabilizer of the invention. It is well-known for those skilled in the art to select a proper stabilizer in the invention and the amount thereof. In general, the amount of the stabilizer used in the invention is ranged from 1 to 10% by volume of the reverse micelle solution. Preferably, acetyl acetone is used in the invention and accounts for 2 to 5% by volume in the reverse micelle solution.

[0026] The dip coating technique used in the process of the invention is the same as that well-known for those skilled in the art. Detailed information on the dip coating technique can be referred to R. Reisfeld and C. K. Jorgensen, 77 Structure and Bonding; Chemistry: Spectroscopy and Applications of Sol-gel Glass, Springer-Verlag, 1992, Berlin, pp91-95.

[0027] The withdrawal speed in step c) can be adjusted based on the roughness of the substrate surface. The speed is normally set at 2-5mm/s.

[0028] The drying temperature of the wet film in step d) is in general at 80°-120°C, and preferably at 100°C for 0.5-1.5 hours. In this step, the dried film may be calcined at a temperature ranging from 500° to 650°C and preferably at 600°C. The dried film may be calcined for 1 to 6 hours and preferably 1 to 3 hours.

[0029] Substrates used in the invention may be any objects in various shapes. Examples of the substrates include metal, glass, ceramics and the like. Stainless steel is a preferable substrate in the invention. It is believed that the reason lies in Fe ion in the stainless steel can be diffused into TiO<sub>2</sub> thin film when calcined, and the presence of Fe (III) will help charge separation and avoid the recombination of the electrons with holes.

[0030] In the invention, after the substrate is dipped into the reverse micelle solution, a homogenous TiO<sub>2</sub> sol-gel layer is formed onto the surface of the substrate with the dip coating technique. A homogenous mesoporous TiO<sub>2</sub> crystalline thin film will be formed after being calcined.

[0031] The substrate used in the invention is preferably cleaned before thin films are coated to achieve a good affinity between the TiO<sub>2</sub> thin film and the substrate.

[0032] The invention will be further described by the following examples.

#### Example 1

##### Preparation of TiO<sub>2</sub> Thin Films onto the Surface of Stainless Steel

[0033] To 100ml of cyclohexane were added Triton X-100, water, and resultant mixture was stirred for 2 hours to obtain a reverse micelle solution. In the solution, the concentration of Triton X-100 ranged from 0.15 to 0.3M, and the ratio between water and Triton X-100 was 2. In this Example, isopropyl titanate together with 5ml of acetyl acetone was added to the reverse micelle solution. The concentration of the titanate was 0.2M. After resultant solution was continuously stirred for about 1 hour to have isopropyl titanate hydrolyzed in nano-droplets of the reverse micelle solution, the solution became homogenous and optically transparent. Stainless steel of Type 304 was then dipped into the reverse micelle solution and a wet TiO<sub>2</sub> film was formed onto the stainless steel by the withdrawing technique, of which the withdrawal speed was controlled at 4mm/s. The wet film was dried at 100°C for 60 minutes and then was calcined in a muffle roaster respectively for 1, 2, 3, 4,

6, and 8 hours. Afterwards, the substrate was cooled to the room temperature to thereby obtain a series of TiO<sub>2</sub> crystalline thin films.

[0034] Table 1 shows the crystallite size of TiO<sub>2</sub> and the contents of Fe species in thin films that were calcined for different periods of time at 500°C.

Table 1

| Calcination Time (h) | Fe2p3(Fe <sup>3+</sup> ) <sup>a</sup> | Fe2p3(Fe <sup>2+</sup> ) <sup>a</sup> | Crystallite (nm) |
|----------------------|---------------------------------------|---------------------------------------|------------------|
| 1                    | 3.18%                                 | 0.34%                                 | 9.43             |
| 3                    | 4.32%                                 | 0.40%                                 | 9.77             |
| 8                    | 5.48%                                 | 1.21%                                 | 10.28            |

[0035] Polycrystalline X-ray diffraction patterns of TiO<sub>2</sub> thin films on stainless steel calcined for different periods of time in this Example were shown in Fig. 1.

[0036] X-ray photoelectron spectra of Ti in thin films on stainless steel calcined for different periods of time in this invention were shown in Fig. 2.

[0037] X-ray photoelectron spectra of Fe in thin films on stainless steel calcined for different periods of time in this Example were shown in Fig. 3.

[0038] A scanning electron microscope image of a thin film on stainless steel calcined at 500°C for 3 hours in this Example was shown in Fig. 4.

## Example 2

### Preparation of TiO<sub>2</sub> Thin Films on the Surface of Glass

[0039] Thin films onto glass were prepared in the same manner as described in Example 1, except that stainless steel is replaced with glass, and thin films were calcined for 3 hours.

## Experimental Example 1

[0040] The photocatalytic activity of TiO<sub>2</sub> thin films was evaluated by the degradation of acetone in air. The area of TiO<sub>2</sub> thin films used for each experiment was 140 cm<sup>2</sup> in a 7,000ml reactor. Before switching on the ultraviolet source, the equilibrium concentration of acetone was controlled at 400±1ppm, and the initial concentration of water vapor was adjusted to 1.2±0.01vol%, and the temperature was regulated at 25±1°C. The

ultraviolet was generated by a 15W 365nm UV lamp (Cole-Parmer Instrument Co.). The concentrations of carbon dioxide, water vapor and acetone were measured on line with a Photoacoustic IR Multigas Monitor (INNOVA Air Tech Instruments Model 1312, Denmark). The total analysis time for each thin film sample was 100 minutes.

[0041] The thin films prepared in Examples 1 and 2 were analyzed using the above procedure, and results thereof were shown in Figure 5. Figure 5 illustrates that the photocatalytic activity of a TiO<sub>2</sub> thin film on stainless steel was 3 folds as much as that on glass.

### Experimental Example 2

#### Photocatalytic Antibacterial Activity of TiO<sub>2</sub> Thin Films

[0042] Photocatalytic antibacterial activity of TiO<sub>2</sub> thin film was evaluated by killing *Bacillus pumilus* in an aqueous solution under ultraviolet irradiation. 2ml of an aqueous solution of *Bacillus pumilus* having a concentration of  $1 \times 10^7$  CFU/ml was pipetted onto the TiO<sub>2</sub> thin film on stainless steel as prepared in Example 1 (calcined for 3 hours). The stainless steel was illuminated by a 15 W 365nm UV lamp (Cole-Parmer Instrument Co.) at a light intensity of 0.63mW/cm<sup>2</sup>. 20 or 40μl aliquots of serially diluted solutions containing *Bacillus pumillus* were dispensed into 1 ml of phosphate buffer. Resultant solutions were plated on Luria-Bertani (LB) agar plates at 10 or 20 min intervals. The plates were then incubated at 37°C for 24h, and the number of colonies on the plates was counted. The change in the number of bacteria on the surface TiO<sub>2</sub> thin films on stainless steel was calculated.

[0043] Results were shown in Figure 6.

### Experimental Example 3

#### Hydrophilicity of TiO<sub>2</sub> Thin Films

[0044] Hydrophilicity of a TiO<sub>2</sub> thin film was evaluated with a change of the contact angle between water and the thin film under ultraviolet irradiation (15W 365nm, Cole-Parmer Instrument Co.). The contact angle was measured by an instrument, Model CA-XP, Kyowa Interface Science Co. Ltd., Japan. Thin films on stainless steel as prepared in Example 1 were exposed to air for 1 to 2 months to have the contact angle of water on the



thin film increased to 50-60°. Then, the thin films were irradiated by ultraviolet light. The results were shown in Figure 7, which indicated that the contact angle was decreased from 50-60° to around 5° after the thin film was irradiated for 1 hour. It was understood that thin films of the invention had an excellent hydrophilicity.

[0045] It is understood that the above Examples and description are only used to illustrate the invention, and that any varieties or modifications to the present invention without departing from the spirit of the invention will be fallen into the scope of the invention which is defined by appended claims.